# Theory of the first-order isostructural valence phase transitions in mixed valence compounds $YbIn_xAg_{1-x}Cu_4$.

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(February 1, 2008)

For describing the first-order isostructural valence phase transition in mixed valence compounds we develop a new approach based on the lattice Anderson model. We take into account the Coulomb interaction between localized $f$ and conduction band electrons and two mechanisms of electron-lattice coupling. One is related to the volume dependence of the hybridization. The other is related to local deformations produced by $f$ shell size fluctuations accompanying valence fluctuations. The large $f$-state degeneracy allows us to use the $1/N$ expansion method. Within the model we develop a mean-field theory for the first-order valence phase transition in $YbInCu_4$. It is shown that the Coulomb interaction enhances the exchange interaction between $f$ and conduction band electron spins and is the driving force of the phase transition. A comparison between the theoretical calculations and experimental measurements of the valence change, susceptibility, specific heat, entropy, elastic constants and volume change in $YbInCu_4$ and $YbAgCu_4$ are presented, and a good quantitative agreement is found. On the basis of the model we describe the evolution from the first-order valence phase transition to the continuous transition into the heavy-fermion ground state in the series of compounds $YbIn_{1-x}Ag_xCu_4$. The effect of pressure on physical properties of $YbInCu_4$ is studied and the $H-T$ phase diagram is found.

71.27+a,75.20.Hr

## I. INTRODUCTION

The first-order isostuctural valence phase transition observed in rare earth intermetallic compounds is one of the most striking and interesting phenomena in strongly correlated electron systems. For the first time the transition was discovered in elemental Ce which at applied pressure shows a $\alpha \rightarrow \gamma$ transition (for a review, see [1,2]). Other compounds demonstrating the transition are samarium monochalcogenides, [3,4] a few Eu-based compounds, [5,6] $CeNi_xCo_{1-x}Sn$, [7] and $YbInCu_4$. [8–10] The latter compound has attracted much recent attention because $YbInCu_4$ demonstrates a first-order isostructural valence phase transition at ambient pressure. The remarkable peculiarity of the transition lies in the small change of valence of the Yb ions from nearly +3 at high temperatures ($T > 50$ K) to about 2.8-2.9 below the

critical temperature $T_v = 42$ K. The volume expansion of $YbInCu_4$ taking place at $T = T_v$ is also very small, about $+0.5\%$, whereas in Ce the volume change achieves $-15\%$. Despite the small valence and volume changes at $T = T_v$, many physical properties of $YbInCu_4$ are changed dramatically. Already first magnetic measurements [9,10] showed that at the transition the susceptibility drops abruptly, and the Curie-Weiss temperature dependence above $T_v$ is replaced by an almost temperature independent behavior which is typical for a nonmagnetic metal with an enhanced Pauli paramagnetic susceptibility. While the Curie-Weiss behavior at high temperatures can be easily related to the magnetic moment $J = 7/2$ of trivalent Yb ions, the formation of the Pauli paramagnetic state is less clear, taking into account that the valence change $\Delta N_f$ at $T_v$ is estimated to be only about 0.1 as it was revealed by x-ray absorption measurements at the Yb $L_3$ edge. [9,11] From the same point of view the results of Hall effect measurements [11,12] look very amazing, since they give evidence for a very large change of the charge carrier concentration from 0.07 per formula unit at high temperatures to 2.2 per formula unit below $T_v$. In the high temperature phase the Hall measurements are consistent with the band calculations [13] which showed that in this phase $YbInCu_4$ has a semimetal band structure similar to $LuInCu_4$. Transport measurements in $YbInCu_4$ also shows that the compound is semimetalic above $T_v$. [14] Resistance measurements revealed a large and abrupt drop of electrical resistivity when decreasing the temperature below $T_v$. Investigations of Cu nuclear quadrupolar resonance [15–17] (NQR) and Cu and In Knight shift [18] in $YbInCu_4$ show that at $T > T_v$ the $4f$ electrons are localized and interact weakly with the conduction band electrons while at $T < T_v$ a Fermi-liquid state with delocalized Yb $4f$ electrons is formed. The measurements revealed occurrence of a strong hybridization between Yb $4f$ electron states and conduction band states in the Fermi-liquid state. This result is in agreement with Mössbauer experiments [9] that also revealed a nonmagnetic state of the Yb ions below $T_v$. Additional evidence for the fact comes from the temperature behavior of the entropy ($S$) inferred from specific heat measurements. [19] Above $T_v$ the entropy is large and can be explained by a large contribution from the $f$ electrons. At $T_v$ the entropy drops significantly and

with decreasing temperature it tends to zero in the limit $T \rightarrow 0$. It means that at $T = 0$ the ground state of the electron system consisting of conduction band and $f$ electrons, is a singlet state which in accordance with magnetic, NQR and transport measurements is a Fermi-liquid state.

Summarizing, one can conclude that the main mystery of YbInCu$_4$ is in the following. In spite of a small valence change at the phase transition ($\Delta N_f \sim 0.1$) from which one could expect that $f$ electrons would save their localized character, the thermal, magnetic, NQR and transport measurements mentioned above clearly demonstrate that below $T_v$ the $f$ electrons loose their localized character and form a nonmagnetic Fermi-liquid state together with the conduction electrons .

Taking into account the nonmagnetic character of the Yb ions at $T < T_v$ , the enhanced values of the zero temperature susceptibility $\chi(0)$ and linear specific heat coefficient $\gamma$, Felner et al. [9] came to the conclusion that YbInCu$_4$ is a "light heavy-fermion system".

The uniqueness of the first-order valence phase transition in YbInCu$_4$ becomes especially clear when we compare the compound with other isostructural Yb compounds, namely, YbXCu$_4$ with X=Ag, Au, Cd, Mg, Tl, and Zn. A detailed study and comparison of the compounds have recently been performed by Sarrao et al. [20] Though the compounds have the same face-centered-cubic crystal structure, their physical properties are very different. Among the compounds YbAgCu$_4$ is of special interest. It is a typical heavy-fermion (HF) compound with no magnetic order. A substitution of Ag by In results in crossover from the HF behavior to the first-order isostructural valence phase transition, as it has been found when investigating the series of compounds YbIn$_{1-x}$Ag$_x$Cu$_4$. [21,22,11]

In order to explain the valence phase transition in Ce several models have been proposed. In the framework of promotional models [23,24] it is assumed that there is an explicit change of the electronic configuration of Ce ions from $4f^1$ to $4f^0$, and $f$ electrons transfer into the conduction band. A Mott transition picture considers the valence transition as a localization-delocalization transition in the system of $f$ electrons. [25] The Kondo volume-collapse (KVC) model [26,27] explains the valence phase transition by a strong volume dependence of the Kondo temperature $T_k$, neglecting correlation effects between the Kondo effect on different $f$ ions. Each of the models has advantages and shortcomings. The shortcomings becomes especially contrasting when we try to use the models for explaining an evolution of the valence phase transition in the series of compounds YbIn$_{1-x}$Ag$_x$Cu$_4$.

The promotional models demand the valence change to be about 1, while in YbIn$_{1-x}$Ag$_x$Cu$_4$ the change is only about 0.1. This disagreement does not allow within the models to explain quantitatively, using realistic physical parameters, magnetic and other properties of the Yb compounds in the low temperature phase. A recent attempt [28] to correct the deficiency of the Falicov-Kimbal

model is based on the assumption that only a fraction of Yb ions are active and other ones are strongly hybridized. However, the assumption has no experimental confirmation. It contradicts , for example, recent thermoanalytical investigations [29] of the system Yb-In-Cu which showed that by choosing certain starting compositions one can obtain such YbInCu$_4$-samples which have $T_v \approx 40$ K, an improved site order and a reduced probability of Yb ions to occupy In-sites. The Falicov-Kimbal model assumes that the $4f^{14}$configuration is the ground state of Yb ions and $4f^{13}$ configuration is the first excited state. This assumption contradicts with a large number of experimental data that give direct and indirect evidences for the fact that the $4f^{13}$ state is the ground state, and the $4f^{13}$ configuration is the first excited state (see below Sec.II). The promotional model actually neglects a hybridization between $f$ states and conduction band states. It contradicts with experimental data on NQR [15–17] and the Knight shift measurements [18] mentioned above. Moreover, on the basis of the models it is impossible to explain the development of a continuous transition into the HF ground state in YbIn$_{1-x}$Ag$_x$Cu$_4$ at $x > 0.2$ [22], as the Kondo effect taking place in the compounds, can not be described in the framework of the model.

In terms of the Mott transition picture [25] at $T < T_v$ the $f$ band width $W$ has to become larger than the on-site Coulomb repulsion energy $U$ between $f$ electrons. It is possible if the volume of the lattice shrinks below $T_v$. Such a situation takes place in Ce, but not in YbInCu$_4$ . The volume of YbInCu$_4$ increases by 0.5%, which evidences against the Mott transition picture.

It should be mentioned that both the promotional models and Mott transition picture have a charge fluctuation energy as the energy scale. Usually a charge fluctuation energy is too large to provide a convincing explanation of the small energy scales observed in YbIn$_{1-x}$Ag$_x$Cu$_4$.

The KVC model faces a serious problem when explaining pressure dependence of the zero temperature susceptibility in YbInCu$_4$. The model needs the Grüneisen parameter $\Gamma$ to be negative and equal to $-3000$, an unphysical value, while the experiment [19] gives $\Gamma \approx -31$. The negative sign of $\Gamma$ also constitutes a challenge to the model because within the usual mechanism of the volume dependence of the Kondo temperature due to the volume dependence of the hybridization, $\Gamma$ should be positive. Moreover, the KVC model neglects correlations, or in other words, coherence in the Kondo screening of nearby Yb ions in the low temperature phase. However, it is the latter effect that results in the formation of the heavy fermion state in a heavy fermion compound such as YbAgCu$_4$(see, for example, reviews [30,31]).

In the present paper we propose a new theoretical approach that allows us both to obtain quantitative agreement with various experimental data and to avoid contradictions and deficiencies of the previous approaches. Our approach is based on the conclusion obtained from

the experimental data mentioned above that the low temperature phase of $YbIn_{1-x}Ag_xCu_4$ is the HF state. From this point of view the first-order valence phase transition is a normal metal (semimetal)-HF metal transition. Besides, it is supposed that at $T > T_v$ in the normal state the $f$ electrons are localized on the $f$ shells and produce the magnetic moments $J = 7/2$ of the Yb ions. In the HF state, i.e. at $T < T_v$, $f$ states are strongly hybridized with conduction band states, and as a result, quasiparticles near the Fermi surface have a hybrid character and an enhanced mass. Such a physical picture can be successfully described on the basis of the lattice Anderson model. However, it is important to note that the conventional lattice Anderson model allows to study only a continuous transition from the normal state with the incoherent Kondo scattering into the heavy-fermion state with the coherent Kondo effect, as it occurs in heavy-fermion compounds. [30] In the present paper we extend the model in the following way. At first, we take into account a Coulomb repulsion between $f$ and conduction band electrons. Second, we take into account two mechanisms of the electron-lattice coupling. The first mechanism is related to the volume dependence of the hybridization between $f$ and conduction band states due to a change of the overlapping between wave functions of the conduction band and $f$ electron states. It is the conventional mechanism of the electron-lattice interaction in HF compounds, that has been used specifically in the KVC model. However, it is necessary to note that valence fluctuations of the Yb ions are accompanied by fluctuations of the $f$ shell size, which results in local lattice deformations. It is the second ($f$-shell-size-fluctuation) mechanism of the electron lattice coupling considered in our approach. If one neglects crystal field splitting, then the $f$ level has the degeneracy $N = 2J + 1 = 8$. Such a large degeneracy enables us to use the $1/N$ expansion technique for attacking the extended lattice Anderson model. In the present work we shall calculate the free energy in the mean-field approximation, that corresponds to the leading order in $1/N$. A calculation of $1/N$ corrections is beyond the scope of our paper.

Our paper has the following structure. In Sec. II we introduce the extended lattice Anderson model. The mean-field approach for studying the model is developed in Sec. III. The electron-lattice coupling and volume change are considered in Sec. IV. In the next Sec. V we investigate magnetic properties of the system and magnetic field effect. Results of numerical calculations based on the mean field approach are discussed in Sec. VI where we compare the theoretical results on temperature and pressure dependences of thermal, magnetic and elastic properties of $YbInCu_4$ and $YbAgCu_4$ with experimental measurements. In Sec.VII we will discuss the role of fluctuations around the mean-field solution in low and high temperature phases and make conclusions..

## II. MODEL

A number of experimental data give direct evidences for the fact that Yb ions in $YbInCu_4$ fluctuate between the magnetic ground state $Yb^{+3}$ having the configuration $4f^{13}$ with one hole in the $f$ shell and total magnetic moment $j=7/2$, and the excited nonmagnetic state $Yb^{+2}$ having a completely filled $f$ shell with the configuration $4f^{14}$. One can mention the Mössbauer spectroscopy [9] and the photoemission spectra (PES) measurements [32]. Moreover, according to the PES measurements, neither $4f^{12}$ nor $4f^{13}$ $^2F_{5/2}$ contribute to low energy properties. Therefore, one can neglect transitions into these states.

For describing the system it is convenient to use a hole representation. Valence fluctuations of Yb ions can be described in terms of hole transitions between $f$ shells and the hole conduction band. The picture of behavior of an $4f$ ion in a metal was developed by Hirst [33]. It underlies the theoretical model we will use in the paper. The system of interacting $f$ holes and conduction band holes can be described using the lattice Anderson Hamiltonian in the slave boson representation: [30,34,35]

$$H_A = \sum_{a\mathbf{k}} \varepsilon_{\mathbf{k}} c_{\alpha\mathbf{k}}^+ c_{\alpha\mathbf{k}} + \sum_{\alpha n} E_f f_{\alpha n}^+ f_{\alpha n} + \sum_{\alpha n} (V b_n^+ c_{\alpha n}^+ f_{\alpha n} + H.c.), \qquad (1)$$

where $c_{\alpha\mathbf{k}}^+$ and $c_{\alpha\mathbf{k}}$ are creation and annihilation operators of conduction band holes with $z$-component $\alpha$ of the total magnetic moment, $\alpha = -j, -j + 1, ...j$, and wave vector $\mathbf{k}$. Operators $f_{\alpha n}^+$ and $f_{\alpha n}$ create and annihilate $f$ holes on a lattice site with a number $n$. The Bose operators $b_n^+$ and $b_n$ are the conventional slave bosons. A wave function of the state with one boson on a site $n$ is equal to $b_n^+ \mid O >$. This state corresponds to the $4f^{14}$ configuration of the $Yb^{+2}$ ion on the site $n$. The operator $b_n^+ b_n$ determines the probability to find the $f$ ion in the divalent state. In order to admit valent fluctuations only between $Yb^{+3}$ and $Yb^{+2}$ states the following constraint is imposed on each lattice site:

$$b_n^+ b_n + \sum_{\alpha} f_{\alpha n}^+ f_{\alpha n} = 1. \qquad (2)$$

We should mention that in the limit $\mu - E_f << \pi |V|^2 \rho_0$ ($\mu$ is the chemical potential and $\rho_0$ is a conduction band density of states) one can integrate over the bosons. As a result, this model becomes the $SU(N)$ periodic Coqblin-Schrieffer model with an exchange interaction $J = |V|^2 /(\mu - E_f)$: [30,38]

$$H_A = \sum_{a\mathbf{k}} \varepsilon_{\mathbf{k}} c_{\alpha\mathbf{k}}^+ c_{\alpha\mathbf{k}} - J \sum_{\alpha\beta n} (c_{\alpha n}^+ f_{\alpha n})(f_{\beta n}^+ c_{\beta n}) \qquad (3)$$

This model describes the integral valence case when the $f^{13}$ state behaves like a spin interacting antiferromagnetically with conduction band holes. In mixed-valence

compounds $E_f$ can be close to $\mu$, i.e. $\mu - E_f \sim \pi |V|^2 \rho_0$. [31] Therefore, in the latter case it is necessary to use the lattice Anderson model.

When a $f$ hole transits into the conduction band, then a corresponding Yb ion acquires an excess negative charge ($\delta q = e$). The excess charge produces a Coulomb potential that attracts conduction band holes. Due to the small charge carrier concentration ($N_{0c} = 0.07$ per formula unit) the interaction is not completely screened. At least, the Coulomb interaction between the fluctuating charge of Yb ions and electrons (or holes) on neighboring Cu ions of which $p$ and $d$ states mainly contribute to the formation of the conduction band, should be taken into account. Unfortunately, a detailed consideration of the long range Coulomb interaction is a complicated problem. For the sake of simplicity we approximate the interaction by use of an on-site Coulomb attraction between the excess charge and conduction holes. The same approximation is made within the promotional models. [23,24] In the slave boson representation this on-site attraction can be written as follows:

$$H_C = -U_{cf} \sum_{\alpha n} b_n^+ b_n c_{\alpha n}^+ c_{\alpha n}, \qquad (4)$$

where the parameter $U_{cf} > 0$. It characterizes the effective value of the Coulomb interaction between $4f$ and conduction band holes. Using the constraint Eq.(2), one can rewrite the interaction in the form

$$H_C = U_{cf} \sum_{\alpha \beta n} f_{\beta n}^+ f_{\beta n} c_{\alpha n}^+ c_{\alpha n} - U_{cf} \sum_{\alpha n} c_{\alpha n}^+ c_{\alpha n} \qquad (5)$$

The first term describes an on-site Coulomb repulsion between conduction band and $f$ holes. The second term results in an energy shift of the conduction band. According to the representation (5), the attractive interaction Eq.(4) is equivalent to the on-site repulsion between conduction band and $f$ electrons. In the present paper we prefer to use the representation Eq.(4).

The total Hamiltonian of the system under consideration is given by

$$H = H_A + H_C. \qquad (6)$$

The model described by the Hamiltonian can be solved exactly in the limit of large degeneracy $N = 2j + 1 >> 1$ if we suppose the following dependence of the parameters $V$ and $U_{cf}$ on $N$:

$$V = \widetilde{V} N^{-1/2}, \; U_{cf} = \widetilde{U}_{cf} N^{-1}, \qquad (7)$$

where $\widetilde{V}$ and $\widetilde{U}_{cf}$ are finite in the limit $N >> 1$. Moreover, it has to be supposed that the initial number of conduction band holes, $n_{0c} = N_{0c}/N$, and the number of $f$ holes, $n_{0f} = N_{0f}/N$, per unit cell and orbital are finite in the limit $N >> 1$. The constrain Eq.(2) must be replaced by the following one: [36]

$$b_n^+ b_n + \sum_{\alpha} f_{\alpha n}^+ f_{\alpha n} = N n_{0f} , \qquad (8)$$

where $n_{0f} = 1/8$ for the considered Yb system.

The partition function of the model Eq.(6) may be written as a path integral over Grassmann variables $c^+$, $c$, $f^+$, $f$ and Bose variables $b^+$, $b$ and $\lambda$ :

$$Z = \int D(c^+ c f^+ f b^+ b \lambda) \exp(-\int_0^\beta d\tau L(\tau)). \qquad (9)$$

Here the Lagrangian $L$ is given by

$$L(\tau) = \sum_{a\mathbf{k}} c_{\alpha\mathbf{k}}^+ (\partial_\tau + \varepsilon_\mathbf{k} - \mu) c_{\alpha\mathbf{k}} + \sum_n b_n^+ \partial_\tau b_n$$
$$+ \sum_{\alpha n} \{ f_{\alpha n}^+ (\partial_\tau + E_f - \mu) f_{\alpha n} + (V b_n^+ c_{\alpha n}^+ f_{\alpha n}$$
$$+ H.c.) - U_{cf} b_n^+ b_n c_{\alpha n}^+ c_{\alpha n} \} + \sum_n i\lambda_n (b_n^+ b_n$$
$$+ \sum_\alpha f_{\alpha n}^+ f_{\alpha n} - N n_{0f}), \qquad (10)$$

where all variables $c_{\alpha n}^+$, $c_{\alpha n}$, $f_{\alpha n}^+$, $f_{\alpha n}$ , $b_n^+$, $b_n$ and $\lambda_n$ are functions of the imaginary time $\tau$. Let us use the following transformation :

$$\exp(U_{cf} \sum_{\alpha n} \int_0^\beta b_n^+ b_n c_{\alpha n}^+ c_{\alpha n} d\tau) =$$

$$U_{cf} \pi^{-1} \int D\Psi_n D\Psi_n^* \exp(-U_{cf} \sum_n \int_0^\beta (\Psi_n \Psi_n^*$$
$$+ \Psi_n b_n^+ b_n + \Psi_n^* \sum_\alpha c_{\alpha n}^+ c_{\alpha n}) d\tau, \qquad (11)$$

where $\Psi_n(\tau)$ and $\Psi_n^*(\tau)$ are complex conjugate Bose variables. Then, substituting this transformation into Eq.(10), we obtain the partition function as a path integral over the Grassmann variables $c_{\alpha n}^+$, $c_{\alpha n}$, $f_{\alpha n}^+$, $f_{\alpha n}$ and Bose variables $b_n^+$, $b_n$, $\Psi$, $\Psi^*$ and $\lambda_n$. The integration over the Bose variables can be performed using the saddle-point method that gives an exact solution of the model with the Hamiltonian (6) in the limit $N \to \infty$. We look for an uniform saddle-point solution:

$$i\lambda_n(\tau) = \lambda, \quad b_n(\tau) = b,$$
$$\Psi_n(\tau) = \Psi, \; \Psi_n^*(\tau) = \widetilde{\Psi}. \qquad (12)$$

Here it should be noted that in the saddle point the $\widetilde{\Psi}$ is not complex conjugate to $\Psi$, i.e. $\Psi^* \neq \widetilde{\Psi}$, because $\mathrm{Re}\Psi$ and $\mathrm{Im}\Psi$ must be considered as independent variables. The physical meaning of $b$ , $\Psi$ and $\widetilde{\Psi}$ becomes clear from the mean field equations:

$$b = -\frac{V}{(\lambda + U_{cf}\Psi) N_u} \sum_{\alpha\mathbf{k}} \langle c_{\alpha\mathbf{k}}^+ f_{\alpha\mathbf{k}} \rangle_{MF} , \qquad (13)$$

4

$$\Psi = -\sum_\alpha \left\langle c_{\alpha n}^+ c_{\alpha n} \right\rangle_{MF} = -N_c, \qquad (14)$$

$$\widetilde{\Psi} = -\left| b \right|^2 , \qquad (15)$$

where $N_u$ is the number of unit cells in the lattice, $N_c$ is the number of conduction band holes per unit cell , $< ... >_{MF}$ means averaging over the mean-field Hamiltonian $H_{MF}$ that easily follows from Eqs.(10)-(15):

$$H_{MF} = \sum_{a\mathbf{k}} \{ (\varepsilon_\mathbf{k} - U_{cf} \left| b \right|^2) c_{\alpha\mathbf{k}}^+ c_{\alpha\mathbf{k}} + \varepsilon_f f_{\alpha\mathbf{k}}^+ f_{\alpha\mathbf{k}}$$
$$+ (Vb^* c_{\alpha\mathbf{k}}^+ f_{\alpha\mathbf{k}} + H.c.) \} - N_u (\varepsilon_f - E_f) N_f, \quad (16)$$

where $\varepsilon_f$ is the renormalized $f$ level energy:

$$\varepsilon_f \equiv E_f + \lambda , \qquad (17)$$

$N_f \equiv \sum_\alpha \langle f_{\alpha n}^+ f_{\alpha n} \rangle$ is the average number of $f$ holes on the $f$ shell on the site $n$. The parameter determines the valence ($\nu$) of the $f$ ion. For example, for an Yb ion we have $\nu = 2 + N_f$. Below, for the sake of simplicity we shall assume that there is only one Yb ion per unit cell. The order parameter $b$ describes the formation of the HF state (in other words, the coherent Kondo state). According to the constraint Eq.(2) (or Eq.(8)) there is the following relation between $b$ and a valence change ($\Delta N_f$) of $f$ ions:

$$\left| b \right|^2 = N n_{0f} - \sum_\alpha \left\langle f_{\alpha n}^+ f_{\alpha n} \right\rangle = N_{0f} - N_f \equiv \Delta N_f \quad (18)$$

Because in the HF state $\left| b \right| \neq 0$, we come to the very important conclusion that in the HF state $f$ ions have a non-integral valence. For example, for Yb ions we have $N_{0f} = 1$, and the valence is equal to $\nu = 3 - \Delta N_f$. Strictly speaking, due to valence fluctuations governed by the hybridization terms in the Anderson Hamiltonian Eq.(1), even in the high temperature region where $\langle b_n \rangle = 0$ the valency is not integral, i.e. $N_f = N_{0f} - \langle b_n^+ b_n \rangle < N_{0f}$, because $\langle b_n^+ b_n \rangle \neq 0$. In order to take into account the effect it is necessary to go beyond the mean-field approach and calculate $1/N$ corrections.

It is convenient instead of the dimensionless order parameter $b$ to use the following energy parameter characterizing the effective hybridization:

$$B \equiv V^* b . \qquad (19)$$

Inserting Eq.(19) into Eq.(18) gives a useful relation:

$$\left| B \right|^2 = \left| V \right|^2 \Delta N_f . \qquad (20)$$

Then Eq.(13) takes the conventional form:

$$B = -\frac{J}{N_u} \sum_{\alpha\mathbf{k}} \left\langle c_{\alpha\mathbf{k}}^+ f_{\alpha\mathbf{k}} \right\rangle , \qquad (21)$$

where the exchange interaction $J$ is given by:

$$J = \frac{\left| V \right|^2}{\varepsilon_f - E_f - U_{cf} N_c}. \qquad (22)$$

From Eq.(16) it follows that the interaction $U_{cf}$ leads to the energy shift $U_{cf}\Delta N_f$ of the conduction band to lower energies. This in turn shifts the chemical potential $\mu$ and effective energy $\varepsilon_f$ with respect to their bare values $\mu_0$ and $\varepsilon_{0f}$.

In accordance to Eq.(22) the interaction $U_{cf}$ influences the exchange interaction $J$, which in turn effects on the Kondo screening. This effect plays a very important role and will be discussed below in detail. From the physical point of view the effect is related to the renormalization of the energy of the first excited state of Yb ions due to the Coulomb interaction.

The diagonalization of the Hamiltonian $H_{MF}$ shows that in the HF state the renormalized band structure consists of two hybrid bands:

$$\widetilde{E}_{\eta\mathbf{k}} = \frac{1}{2} \{ \varepsilon_\mathbf{k} + \widetilde{\varepsilon}_f \mp [(\varepsilon_\mathbf{k} - \widetilde{\varepsilon}_f)^2 + 4 \left| B \right|^2]^{1/2} \}. \qquad (23)$$

where the upper and lower signs corresponds to $\eta = 1$ and 2, respectively, and the following energy parameters are introduced:

$$\widetilde{\varepsilon}_f \equiv \varepsilon_f + U_{cf}\Delta N_f,$$
$$\widetilde{E}_{\eta\mathbf{k}} = E_{\eta\mathbf{k}} + U_{cf}\Delta N_f, \qquad (24)$$
$$\widetilde{\mu} \equiv \mu + U_{cf}\Delta N_f.$$

The free energy of the system is determined by the well known equation:

$$F = E - ST \qquad (25)$$

The internal energy $E$ and entropy $S$ of the electron system per unit cell (or per $f$ ion, because we assume that there is only one $f$ ion per unit cell) is equal to

$$E = \frac{N}{N_u} \sum_{\eta=1,2} \sum_\mathbf{k} \widetilde{E}_{\eta\mathbf{k}} f(\widetilde{E}_{\eta\mathbf{k}}) - U_{cf}\Delta N_f N_t \qquad (26)$$
$$-(\varepsilon_f - E_f) N_f,$$

$$S = -\frac{N}{N_u} \sum_{\eta=1,2} \sum_\mathbf{k} \{ f(\widetilde{E}_{\eta\mathbf{k}}) \ln f(\widetilde{E}_{\eta\mathbf{k}}) \qquad (27)$$
$$+ (1 - f(\widetilde{E}_{\eta\mathbf{k}})) \ln(1 - f(\widetilde{E}_{\eta\mathbf{k}})) \},$$

where

$$N_t = N_c + N_f = N_{0c} + N_{0f} \qquad (28)$$

is the total number of holes per unit cell, and $f(\widetilde{E}) = (\exp((\widetilde{E} - \widetilde{\mu})/T) + 1)^{-1} = f(E)$. It is interesting to note that $N_c = N_{0c} + \Delta N_f$, which demonstrates the fact that a certain part of holes from $f$ shells transit into the conduction band.

## III. MEAN-FIELD EQUATIONS

The state of the system at any temperature $T$ is completely determined by three parameters: $\widetilde{\mu}$, $B$ and $\widetilde{\varepsilon}_f$. To determine the parameters it is necessary to solve a set of three nonlinear mean-field equations:

$$N_t = \frac{1}{N_u} \sum_{\alpha \mathbf{k}} \left( \langle c_{\alpha \mathbf{k}}^+ c_{\alpha \mathbf{k}} \rangle + \langle f_{\alpha \mathbf{k}}^+ f_{\alpha \mathbf{k}} \rangle \right), \qquad (29)$$

$$N_f = \frac{1}{N_u} \sum_{\alpha \mathbf{k}} \langle f_{\alpha \mathbf{k}}^+ f_{\alpha \mathbf{k}} \rangle, \qquad (30)$$

$$B = -\frac{J}{N_u} \sum_{\alpha \mathbf{k}} \langle c_{\alpha \mathbf{k}}^+ f_{\alpha \mathbf{k}} \rangle. \qquad (31)$$

At arbitrary $T$ the mean-field equations have a trivial solution $B = 0$. Moreover, nontrivial solutions with $B \neq 0$ can also exists. These solutions correspond to either minimum or maximum of the free energy $F$. In the case $B \neq 0$ one can rewrite the mean-field equations in a form:

$$N_t = N \int d\varepsilon \rho(\varepsilon) (f(\widetilde{E}_{1\mathbf{k}}) + f(\widetilde{E}_{2\mathbf{k}})), \qquad (32)$$

$$N_f = N \int d\varepsilon \rho(\varepsilon) \frac{|B|^2 f(\widetilde{E}_{1\mathbf{k}}) + (\widetilde{\varepsilon}_f - \widetilde{E}_{1\mathbf{k}})^2 f(\widetilde{E}_{2\mathbf{k}})}{|B|^2 + (\widetilde{\varepsilon}_f - \widetilde{E}_{1\mathbf{k}})^2}, \qquad (33)$$

$$\frac{1}{J} = N \int d\varepsilon \rho(\varepsilon) \frac{f(\widetilde{E}_{1\mathbf{k}}) - f(\widetilde{E}_{2\mathbf{k}})}{\widetilde{E}_{2\mathbf{k}} - \widetilde{E}_{1\mathbf{k}}}, \qquad (34)$$

where $\rho(\varepsilon)$ is the density of states (DOS) in the conduction band:

$$\rho(\varepsilon) = \frac{1}{N_u} \sum_{\mathbf{k}} \delta(\varepsilon - \varepsilon_{\mathbf{k}}). \qquad (35)$$

It is convenient to represent the internal energy $E$, Eq.(26), as follows:

$$E = N \sum_{\eta=1,2} \int d\varepsilon \rho(\varepsilon) \widetilde{E}_{\eta \mathbf{k}} f(\widetilde{E}_{\eta \mathbf{k}}) + \frac{1}{J} |B|^2$$
$$+ \frac{U_{cf}}{|V|^4} |B|^4 - (\widetilde{\varepsilon}_f - E_f) N_{0f}. \qquad (36)$$

Let us analyze the exchange interaction $J$ given by Eq.(22). Using the relations $N_c = N_{0c} + \Delta N_f$ and Eq.(20), one can rewrite $J^{-1}$ in the form:

$$\frac{1}{J} = \frac{1}{|V|^2} \left( \widetilde{\varepsilon}_f - E_f - U_{cf} N_{0c} - \frac{2 U_{cf} B^2}{|V|^2} \right) \qquad (37)$$

Eq.(37) shows that in the HF state, i.e. at $B \neq 0$, the exchange interaction $J$ is enhanced with respect to one in the normal state with $B = 0$. It is the effect that is the driving force of the first-order valence phase transition in YbInCu$_4$ as it will be shown below.

In the case $U_{cf} = 0$ at $T < T_k$ the mean-field equations Eqs.(32)-(34) have only one nontrivial solution with $B \neq 0$ which describes a continuous transition into the HF state. We call the solution "conventional". The Kondo temperature $T_k$ can be found from Eq.(34), supposing $B = 0$. A detailed analysis of the HF state described by the conventional solution can be found, for example, in the review. [30] Temperature behavior of $\Delta N_f$ and susceptibility in the HF state found from a numerical solution of Eqs.(32)-(34) will be discussed below in Sec. VI.

One can consider the formation of the Fermi-liquid state with a non-zero effective hybridization $B$ as a coherent Kondo effect . [30] The mean-field theory enables us to find the leading contribution in terms the $1/N$ expansion into the phenomena. In the high temperature region the mean-field solution with $B = 0$ discribes a localized $f$ holes that do not interact with conduction holes. To take into account the interaction it is necessary to consider $1/N$ corrections due to slave boson fluctuations around the mean-field solution. The corrections can be important in the region of crossover from a weak coupling regime to a strong coupling regime that occurs at $T \sim T_k$. [37]

In addition, one can note that at $T = T_k$ the Green's function $< b_n^+(i\omega) b_n(i\omega) >$ has a pole at $\omega = 0$. It is the singularity that results in the Abrikosov-Suhl resonance.

At low temperatures $T << T_k$ in the HF state a new energy scale arises. It is the so called low temperature Kondo scale $T_0$ determined as

$$T_0 \equiv \widetilde{\varepsilon}_f - \widetilde{\mu}. \qquad (38)$$

Solving Eq.(34) at $T = 0$ in the case $\rho(\varepsilon) = \rho_0$ gives

$$T_0 = (\widetilde{\varepsilon}_f - \widetilde{E}_{\min}) \exp(-\frac{1}{N \rho_0 J}) \qquad (39)$$

where $\widetilde{E}_{\min} = \widetilde{E}_1(k = 0)$. It is important to note a difference between the two Kondo scales $T_0$ and $T_k$. But the Abrikosov-Suhl resonance, the Kondo temperature $T_k$ appears also in a high-temperature expansion of the spin susceptibility, for example, and other physical parameters in the weak coupling regime. $T_0$ is an energy scale that determines thermodynamic properties in the Fermi-liquid regime with strong coupling. In general case, $T_0 \neq T_k$ (for a detail discussion on the problem see, for example, a review [38]).

## IV. STRICTION PHENOMENA

When an Yb ion transits from the ground state Yb$^{+3}$ into the excited state Yb$^{+2}$, the radius of the $f$ shell

increases. It results in an local internal pressure that brings about a local lattice strain. Let $e_{ij}$, where $i, j = x, y, z$, be a local strain tensor. Since the probability to find an Yb ion on the site $n$ in the divalent state is given by the operator $b_n^+ b_n$, we can write the energy related to this type of the electron-lattice interaction in the form

$$H_{e-l} = -\sum_n d_{ij} e_{ji}(n) b_n^+ b_n. \tag{40}$$

For a cubic lattice the energy tensor $d_{ij}$ has a simple form $d_{ij} = \delta_{ij} d$, therefore this electron-lattice interaction can be rewritten as:

$$H_{e-l} = -d \sum_n e_B(n) b_n^+ b_n. \tag{41}$$

where $e_B(n) = e_{xx}(n) + e_{yy}(n) + e_{zz}(n)$ is a local volume strain. For Yb compounds the interaction energy $d$ is positive, which corresponds to a local volume expansion when Yb ions change their valence from $+3$ to $+2$. In turn, $d$ is negative for Ce ions with the ground state configuration $4f^1$, because the $f$ shell of a Ce ion in the excited $4f^0$ state has a smaller radius than in the $4f^1$ state. In order to make clear a physical meaning of the interaction $H_{e-l}$ let us find an average value $< H_{e-l} >$ in the case of an uniform strain $e_B(n) = e_B$. Taking into account Eq.(18) we find

$$< H_{e-l} > = -d e_B \Delta N_f N_u \tag{42}$$

The volume strain $e_B$ is related to the volume change $(\Delta v)$ of the whole volume $(v)$, namely, $e_B = \Delta v / v$. Then Eq.(42) takes the form

$$< H_{e-l} > = p_0 \Delta N_f \Delta v \tag{43}$$

where we introduce a new fundamental parameter

$$p_0 \equiv -d/v_0. \tag{44}$$

Here $v_0$ is the unit cell volume (per $f$ ion). The parameter $p_0$ has the following physical meaning: $p_0$ is a pressure produced by a $f$ ion on the lattice when the $f$ ion valence is changed by 1. $p_0$ is negative for Yb ions, because it tends to expand the lattice, and positive for Ce ions, because it tends to shrink the lattice. The energy Eq.(43) has a simple physical meaning. This is the work produced by the pressure $p_0 \Delta N_f$ in order to change the volume of the system by value $\Delta v$.

Apart of the $f$-shell-size-fluctuation mechanism (Eq.(40)) of the electron-lattice interaction there is another mechanism related to a volume dependence of the hybridization parameter $V$ in Eq.(1):

$$V(e_B) = V \exp(r e_B) \tag{45}$$

where $r < 0$ that corresponds to increasing $V(e_B)$ when decreasing volume. Eq.(45) follows from a volume dependence of overlapping between $f$ and conduction band

wave functions. Usually it is supposed that it is the mechanism that is responsible for a pressure dependence of $T_k$ and the Kondo volume collapse phenomena in compounds with Kondo impurities and HF compounds. However, as we shall show below it is not valid in the case of Yb compounds in which the $f$-shell-size-fluctuation mechanism plays a more important role. Taking into account these two mechanisms of the electron-lattice interaction represented by Eqs.(41) and (45), we obtain the following total Hamiltonian:

$$H = H_A + H_C + H_{e-l} + H_{lat}, \tag{46}$$

where

$$H_{lat} = \frac{1}{2} C_B e_B^2 N_u \tag{47}$$

is the energy of a uniformly deformed lattice. $C_B$ is the bulk modulus per $f$ ion. The Hamiltonian Eq.(46) results in the same mean-field equations (32)-(34) with the only difference. Namely, the exchange interaction $J$ becomes strain dependent:

$$J(e_B) = \frac{|V(e_B)|^2}{\widetilde{\varepsilon}_f - E_f - U_{cf} N_{0c} - 2U_{cf} \Delta N_f - d e_B} \tag{48}$$

Taking into account the elastic energy Eq.(47) and electron energy Eq.(36), the total internal energy per $f$ ion can be written in the form

$$E_t = E + \frac{1}{2} C_B e_B^2. \tag{49}$$

In the equilibrium state the strain $e_B$ is determined by a minimization of the free energy with respect to $e_B$: $\partial F / \partial e_B = 0$. Taking into account Eqs.(48) and (45) the minimization results in an equation:

$$e_B = \left( \frac{d}{C_B} + \frac{2r |V(e_B)|^2}{C_B J(e_B)} \right) \Delta N_f \tag{50}$$

which easily follows from the relation:

$$\partial F / \partial e_B = \partial E_t / \partial e_B$$
$$= |B|^2 \frac{\partial}{\partial e_B} \left( \frac{1}{J(e_B)} \right) + U_{cf} |B|^4 \frac{\partial}{\partial e_B} \left( \frac{1}{|V(e_B)|^4} \right)$$
$$+ C_B e_B$$

since the entropy $S$, Eq.(27), does not depend on $e_B$ in a direct way (here we neglect a volume dependence of the Fermi energy). Eq.(50) shows that the volume strain $e_B$ is proportional to the valence change $\Delta N_f$ of the Yb ions. Such a proportionality have been observed experimentally. [11] Eq.(50) together with Eqs.(32)-(34), where $J$ is replaced by $J(e_B)$, represent a closed set of nonlinear equations which determine the equilibrium parameters $\widetilde{\varepsilon}_f(T)$, $\widetilde{\mu}(T)$, $B(T)$ and $e_B(T)$.

In the case of a sufficiently small strain $|e_B| << 1$ one can use a linear approximation:

$$J(e_B)^{-1} \approx J(0)^{-1} + N\rho_0 \Omega e_B, \qquad (51)$$

where $\rho_0$ is the DOS on the Fermi surface, $\Omega = \Omega_1 + \Omega_2 + \Omega_3$,

$$\Omega_1 + \Omega_2 = \left(\frac{\partial \ln J(e_B)}{\partial \ln v}\right)_{B, \widetilde{\varepsilon}_f, e_B = 0} \qquad (52)$$

$$\Omega_1 = -\frac{2r}{N\rho_0 J}, \quad \Omega_2 = -\frac{d}{N\rho_0 |V|^2}.$$

$$\Omega_3 = \frac{1}{N\rho_0} \left(\frac{\partial J^{-1}}{\partial B}\frac{\partial B}{\partial e_B} + \frac{\partial J^{-1}}{\partial \widetilde{\varepsilon}_f}\frac{\partial \widetilde{\varepsilon}_f}{\partial e_B}\right)_{e_B = 0}$$

Since $r < 0$, consequently, $\Omega_1$ is always positive while $\Omega_2$ can be both positive and negative. In general case $\Omega$ can be both positive and negative. The physical meaning of the parameter $\Omega$ comes from Eq.(39). Substitution of Eq.(51) into Eq.(39) gives

$$T_0(e_B) \sim \exp(-\frac{1}{N\rho_0 J(0)} - \Omega e_B). \qquad (53)$$

The equation determines the dependence of the low temperature Kondo scale $T_0$ on the strain $e_B$.

Electron-lattice interactions described by Eqs.(40) and (45) lead to a renormalization of the elastic constants. In order to find the effect it is necessary to calculate the free energy $F$ as a function of $e_B$ at given $T$: $F = F(T, e_B)$. For this purpose we have to solve Eqs.(32)-(34) with the coupling Eq.(48) at fixed $e_B$. This enables us to find $\widetilde{\varepsilon}_f(T, e_B)$, $\widetilde{\mu}(T, e_B)$ and $B(T, e_B)$ and then $F(T, e_B)$. Renormalized elastic constants $c_{ij}^*$ are equal to

$$c_{ij}^* = \left(\frac{\partial^2 F}{\partial e_{ii}\partial e_{jj}}\right)_{e = e(T)}, \qquad (54)$$

where $e_{ii}(T) = e_B(T)/3$ is the equilibrium elastic strain.

An effect of applied pressure $P$ on the system under consideration can be calculated from the thermodynamic relation

$$P = -\frac{\partial F(v, T)}{\partial v} \qquad (55)$$

Eq.(55) together with Eqs.(32)-(34), where $J$ is replaced by $J(e_B)$, represent a closed set of nonlinear equations that determine the equilibrium parameters $\widetilde{\varepsilon}_f(T, P)$, $\widetilde{\mu}(T, P)$, $B(T, P)$ and $e_B(T, P)$.

## V. MAGNETIC FIELD EFFECT

Let us study an influence of a magnetic field $H$ on the system and the valence phase transition. We shall take into account only an interaction of spins of conduction band and localized $f$ holes with the magnetic field (Zeeman energy). The Zeeman energy of the spins in a magnetic field $H$ directed along $z$ axis is equal to

$$H_z = -g\mu_B H \sum_n (S_{fn}^z + S_{cn}^z), \qquad (56)$$

where $g$ and $\mu_B$ are the gyromagnetic factor and the Bohr magneton, respectively, $S_{cn}^z$ and $S_{fn}^z$ are $z$ components of the spin operators for conduction band and $f$ holes:

$$S_{cn}^z = \sum_{\alpha=-j}^{j} \alpha c_{\alpha n}^+ c_{\alpha n},$$

$$S_{fn}^z = \sum_{\alpha=-j}^{j} \alpha f_{\alpha n}^+ f_{\alpha n}. \qquad (57)$$

The magnetic field splits the $N$-fold degenerate hybrid bands Eq.(23):

$$E_{\eta\alpha\mathbf{k}} = E_{\eta\mathbf{k}} - \alpha g\mu_B H. \qquad (58)$$

Neglecting a magnetic field effect on the orbital motion of heavy fermions, which is possible due to the large mass of the quasiparticles, one can write the mean-field equations (32)-(34) in the form:

$$N_t = \sum_\alpha \int d\varepsilon \rho(\varepsilon)(f(\widetilde{E}_{1\alpha\mathbf{k}}) + f(\widetilde{E}_{2\alpha\mathbf{k}})), \qquad (59)$$

$$N_f = \sum_\alpha \int d\varepsilon \rho(\varepsilon)\frac{|B|^2 f(\widetilde{E}_{1\alpha\mathbf{k}}) + (\widetilde{\varepsilon}_f - \widetilde{E}_{1\mathbf{k}})^2 f(\widetilde{E}_{2\alpha\mathbf{k}})}{|B|^2 + (\widetilde{\varepsilon}_f - \widetilde{E}_{1\mathbf{k}})^2},$$
$$(60)$$

$$\frac{1}{J} = \sum_\alpha \int d\varepsilon \rho(\varepsilon)\frac{f(\widetilde{E}_{1\alpha\mathbf{k}}) - f(\widetilde{E}_{2\alpha\mathbf{k}})}{\widetilde{E}_{2\mathbf{k}} - \widetilde{E}_{1\mathbf{k}}}. \qquad (61)$$

If we take into account the electron-lattice interaction then the exchange interaction $J$ in Eq.(61) is given by Eq.(48). Solving these equations together with Eq.(50), we can find parameters $\widetilde{\varepsilon}_f(T, H)$, $\widetilde{\mu}(T, H)$, $B(T, H)$ and $e_B(T, H)$. Then we can calculate the total internal energy per $f$ ion:

$$E_t = \sum_\alpha \sum_{\eta=1,2} \int d\varepsilon \rho(\varepsilon)\widetilde{E}_{\eta\alpha\mathbf{k}}f(\widetilde{E}_{\eta\alpha\mathbf{k}}) + \frac{1}{J(e_B)}|B|^2$$
$$+ \frac{U_{cf}}{|V(e_B)|^4}|B|^4 - (\widetilde{\varepsilon}_f - E_f)N_{0f} + \frac{1}{2}C_B e_B^2, \quad (62)$$

and the entropy

$$S = -\sum_\alpha \sum_{\eta=1,2} \int d\varepsilon \rho(\varepsilon)\{f(\widetilde{E}_{\eta\alpha\mathbf{k}}) \ln f(\widetilde{E}_{\eta\alpha\mathbf{k}})$$
$$+ (1 - f(\widetilde{E}_{\eta\alpha\mathbf{k}})) \ln(1 - f(\widetilde{E}_{\eta\alpha\mathbf{k}}))\}. \qquad (63)$$

Calculating $F$ as a function of $T, H$ and $e_B$ enables us to find the influence of the magnetic field on the elastic constants Eq.(54).

In the heavy-fermion state the magnetization of the system per unit cell can be given as either a sum over magnetic moments of conduction band and $f$ holes or a sum over magnetic moments of heavy quasiparticles in the hybrid bands Eq.(58):

$$M = g\mu_B N_u^{-1} \sum_n (< S_{cn}^z > + < S_{fn}^z >)$$
$$= g\mu_B \sum_\alpha \sum_{\eta=1,2} \alpha \int d\varepsilon \rho(\varepsilon) f(\widetilde{E}_{\eta\alpha\mathbf{k}}). \qquad (64)$$

Differentiating $M$ with respect to $H$ at $H = 0$ one can find the static magnetic susceptibility per $f$ ion:

$$\chi(T) = -\frac{1}{3}(g\mu_B)^2 j(j+1) N \sum_{\eta=1,2} \int d\varepsilon \rho(\varepsilon) f'(\widetilde{E}_{\eta\mathbf{k}}),$$
$$(65)$$

where $f'(E) = \partial f(E)/\partial E$. Moreover, we took into account that at small magnetic fields the parameters $\widetilde{\varepsilon}_f(T,H)$, $\widetilde{\mu}(T,H)$, $B(T,H)$ and $e_B(T,H)$ have field corrections of order of $O(H^2)$. At $T = 0$ we obtain the well known result (see, for example, the review [30]):

$$\chi(T=0, H=0) = \frac{1}{3}(g\mu_B)^2 j(j+1) N \rho_F^*. \qquad (66)$$

Here the renormalized density of state $\rho_F^*$ and the effective quasiparticle mass $m^*$ on the Fermi surface are given by

$$\frac{\rho_F^*}{\rho_0} = \frac{m^*}{m_0} = 1 + \frac{|B|^2}{T_0^2} \qquad (67)$$

In the right hand side of Eq.(67) the first term is contributed by conduction holes, and the second term is contributed by $f$ holes. [30,38] It is obviously that in the case $m^*/m_0 >> 1$ the zero temperature susceptibility (66) is mainly determined by $f$ holes. In the case $\mu_0 >> T_0$ at $T = H = 0$ from Eqs.(32)-(33) we obtain a useful relation

$$|B|^2 = \frac{N_f T_0}{N \rho_0}. \qquad (68)$$

An additional assumption $N\rho_0 T_0 << 1$ gives the following result: [30]

$$\chi(T=0, H=0) = \frac{1}{3}(g\mu_B)^2 j(j+1) \frac{N_f}{T_0}. \qquad (69)$$

However, the inequality $\mu_0 >> T_0$ can be invalid for a semimetal similar to YbInCu$_4$ having a low charge carrier concentration and large enough $T_0$. Therefore in general case it is better to use Eqs.(66) and (67). If $T_0 >> T_v$ where $T_v$ is the critical temperature of the valence

phase transition, then at $T < T_v$ in the HF state the susceptibility $\chi(T, H = 0)$ will have a weak temperature dependence, as a temperature correction to $\chi(0)$ is of order of $O(T^2/T_0^2)$.

Above $T_v$, that is in the normal paramagnetic state with incoherent Kondo scattering, the total susceptibility of the electron system considered is mainly determined by localized $f$ spins, as at temperatures $T << \mu$ the Pauli susceptibility of conduction holes is much smaller than the susceptibility of the localized $f$ holes weakly interacting with conduction holes. Within the mean-field approach the interaction is neglected, and $f$ holes behave as free paramagnetic spins with the Curie-Weiss susceptibility:

$$\chi(T, H = 0) = \frac{1}{3}(g\mu_B)^2 j(j+1) \frac{N_{0f}}{T}. \qquad (70)$$

This result is valid in the leading order in $1/N$. In order to find logarithmic corrections into $\chi$ due to the Kondo screening, it is necessary to study local fluctuations of slave bosons $b_i$ around the paramagnetic state. [38]

One can conclude that on decreasing the temperature below $T_v$ the susceptibility undergoes a jump from the value Eq.(70) to much the lower value Eq.(66). The result is in qualitative agreement with experimental data (see paper [10] and recent data [19,22]).

## VI. RESULTS OF NUMERICAL CALCULATIONS

In the framework of the mean-field approach to the extended lattice Anderson model at a given temperature $T$ and pressure $P$ the free energy is completely determined by four physical parameters: the chemical potential $\mu$, the effective energy $\varepsilon_f$ of the $f$ level, the order parameter (effective hybridization) $B$ and the volume strain $e_B$. In order to find the parameters we solved numerically the set of equations (32)-(34) and (55) with the exchange energy Eq.(48). For the sake of simplicity we used a flat conduction band with an energy independent DOS $\rho_0$.

We found that, depending on the $f$ level energy $E_f$, the hybridization parameter $V$, the conduction band DOS $\rho_0$, the initial concentration $N_{0c}$ of conduction band holes and the interaction $U_{cf}$, the set of the mean-field equations (32)-(34) and (55) has different solutions that give different scenarios of temperature behavior.

At first let us briefly discuss different solutions in the simplest case when the electron-lattice interaction is neglected and $P = 0$. At $U_{cf} = 0$ and $T > T_k$ the mean-field equations has only a trivial solution with $B = 0$. At $T < T_k$ apart from the trivial solution there is one nontrivial solution with $B \neq 0$, namely, the conventional solution describing a continuous transition into the HF state. The temperature dependence $B(T)$ of the conventional solution is represented in Fig.1 at parameters $N_{0c} = 0.069$, $|V/\mu_0|^2 = 19$ and $1/N\rho_0 J_0 = 3$. At $T < T_k$ the HF state with the $B(T)$ has a lower free energy than

the trivial solution. Solving numerically Eqs.(32)-(34), we have found that at $T = 0$ and $U_{cf} = 0$ within the conventional solution the valence change $\Delta N_f$ can achieve a maximum value of order 0.05.

With increasing $U_{cf}$ at fixed parameters $E_f$, $V$, $\rho_0$ and $N_{0c} \sim 0.07$ the behavior of $\Delta N_f (T)$ remains qualitatively the same as for the conventional solution with $U_{cf} = 0$. There are only quantitative differences which are nevertheless very important. At a certain value of $U_{cf}$ ($U_{cf}/(N\rho_0 |V|^2) \sim 3$) the valence change $\Delta N_f(0)$ can achieve a value of order 0.1. Such a scenario we shall use below for describing the physical properties of YbAgCu$_4$.

At large enough $U_{cf}$ ($U_{cf}/(N\rho_0 |V|^2) \gtrsim 5$ and $N_{c0} \sim 0.07$) in a certain temperature region the mean-field equations (32)-(34) have two nontrivial solutions corresponding to minimums of the free energy $F$ as a function of the effective hybridization $B$ (there are also solutions corresponding to maximums of $F(T,B)$). At parameters $U_{cf}/(N\rho_0 |V|^2) = 5.6$, $N_{0c} = 0.069$, $|V/\mu_0|^2 = 19$ and $1/N\rho_0 J_0 = 3$ (below we shall use these parameters for studying properties of YbInCu$_4$) these solutions are represented in Fig.1. One solution with small $B$ begins at $T = T_k$ , i.e. $B(T_k) = 0$, and ends at a point $s$ at temperature $T_s = 0.83T_k$. We shall call the solution "soft". Near $T_k$ the soft solution behaves similar to the conventional solution. Moreover, there is another solution with larger $B$. It starts at a point $h$ at temperature $T_h \approx 1.06T_k$, exists up to $T = 0$ and has a weak temperature dependence. We call the solution "hard". The free energy $F(T,B)$ as a function of $B$ at different temperatures $T$ is represented in Fig.2. At $T > T_h$ the $F$ has only one minimum at $B = 0$. In the range $T_k < T < T_h$ the $F$ has two minimums, one at $B = 0$ and the other at $B$ corresponding to the hard solution. At $T < T_k$ the trivial solution gives a maximum of $F$. In the range $T_s < T < T_k$ the $F$ has two minimums related to the soft and hard solutions. Below $T_s$ there is only one minimum given by the hard solution. For the given parameters a first-order phase transition takes place at $T_v \approx 0.97T_k$ . At $T > T_v$ either soft or trivial solutions give an absolute minimum of $F$ , while at $T < T_v$ the absolute minimum is given by the hard solution. The valence jump $\Delta N_f$ is of order 0.2. This scenario will be used below for describing the first-order valence phase transition in YbInCu$_4$.

At even larger $U_{cf}$ the order parameter $B$ corresponding to the hard solution can be much larger than $B$ of the soft solution. The hard solution can arises well above $T_k$ since in this case $T_h >> T_k$. The soft solution can exist down to very small temperatures since in this case $T_s << T_k$. Besides, a first-order valence phase transition can occur at a critical temperature $T_v >> T_k$ with the valence change $\Delta N_f(0) \sim 1$. Such a scenario occurs, for example, for the model parameters $U_{cf}/(N\rho_0 |V|^2) = 10$, $N_{0c} = 0.069$, $|V/\mu_0|^2 = 20$ and $1/N\rho_0 J_0 = 4$ which give $T_v/T_k = 130$.

Our analysis of the numerical solutions reveals that there is a correlation between $\Delta N_f(0)$, $T_k$ and $T_v$. If $T_k << T_v$ , which takes place at sufficiently large $U_{cf}$ ($U_{cf}/(N\rho_0 |V|^2) \gtrsim 9$), then $\Delta N_f(0)$ is close to 1. If $T_v$ is only slightly larger than $T_k$, then $\Delta N_f(0) \sim 0.25$. In the frame of the first-order phase transition scenario a minimum value $\Delta N_f(0) \sim 0.2$ is achieved when $T_v$ is slightly smaller than $T_k$.

There are also regions in the parameter space ($E_f$, $V$, $\rho_0, N_{0c}, U_{cf}$) in which even at $U_{cf} \neq 0$ a first-order phase transition does not occur. If the electron-lattice interaction is included then one can expect a rich $T - P - H$ phase diagram.

## A. Physical properties of YbInCu$_4$

Let us apply the numerical calculations discussed above for studying the thermodynamic properties of YbInCu$_4$. For the sake of simplicity we suppose the conduction band to be flat and the degeneracy $N = 8$. In accordance with the Hall measurements [11] we use the initial charge carrier concentration $N_{0c}=0.069$ per formula unit. The best fit to the experimental data is found at the following parameters: $V = 0.267$ eV, $U_{cf} = 0.451$ eV, $N\rho_0=1.125$ eV$^{-1}$, $\mu_0 - E_f = 0.272$ eV. The parameter $N\rho_0 V^2$ characterizing the $f$ level broadening due to the hybridization is calculated to be 0.08 eV. One can note that for rare earth compounds the broadening is typically of order 0.01-0.1 eV. [2] The initial chemical potential $\mu_0$ is calculated to be 0.061 eV. The obtained value of $V$ is in good agreement with the mixing terms 0.27 eV between Yb $4f$ and the Cu $p$ states found in the electronic band structure calculations [13] of YbInCu$_4$. According to the calculations [13], the Cu $p$ states give the main contribution into the $\Gamma_1$ states in the vicinity of the Fermi surface.

The energy of the $4f$ level, $\mu_0 - E_f = 0.272$ eV, is consistent with the experimental results of PES , 0.3 eV, for the compound. [32] One can note that in other Yb based mixed valent compounds such as YbAl$_2$ and YbAl$_3$ the $4f$ level energy estimated from photoemission spectra [41,42] also is not centered at the Fermi energy, but 0.24 eV below it.

For describing electron-lattice interactions it is necessary to set the parameters $r$ and $d$. In many HF compounds the parameter $r$ is of order $-8 < r < -2$. We take $r = -2$ and $d = 2$ eV that give $\Omega_1 \approx 12$ and $\Omega_2 = -25$ in Eq.(52). The unit cell of YbInCu$_4$ contains four Yb ions and has volume $372 \times 10^{-24}$cm$^3$. Therefore each Yb ion occupies volume $v_0 = 93 \times 10^{-24}$cm$^3$. Since according to experimental data [43,44] in the normal state the bulk modulus of YbInCu$_4$ is equal to $11, 1 \times 10^{11}$ erg/cm$^3$, the parameter $C_B$ in Eq.(47) is taken to be equal to $c_B v_0 = 1, 03 \times 10^{-10}$ erg.

Our analysis of the numerical solutions of the mean-field equations (32)-(34) and (55) shows that for the parameters chosen the system under consideration under-

goes a first-order isostructural valence phase transition at the critical temperature $T_v$ =42 K. Above $T_v$ the system is in the normal state. Below $T_v$ the HF state described by the hard solution is formed, as the free energy of the HF state becomes smaller than the free energy of the normal state with the incoherent Kondo scattering. It is demonstrated by Fig.3. Within the mean-field solution at $T > T_v$ the Yb ions have the integral valency +3 corresponding to $B = 0$. At $T < T_v$ the Yb ions have a non-integral valence $3 - \Delta N_f$. A temperature dependence of the $\Delta N_f$ is shown in Fig.4. At $T = T_v$ there is a jump of the valence, $\Delta N_f = 0.24$. With decreasing temperature the valence change $\Delta N_f$ achieves the value 0.27. The value is larger than 0.17 deduced from $L_3$ measurements. [11] Reasons of the discrepancy will be discussed below.

### 1. Thermal properties of YbInCu$_4$

In Fig.5 we represent the temperature behavior of the entropy $(S)$ of the system considered. In the framework of our approach above $T_v$ the entropy is large enough due to a large contribution given by localized $f$ holes. At $T_v$ the entropy drops from $S(T_v + 0) = 25$ J/mol K to $S(T_v - 0) = 4.9$ J/mol K, i.e. $\Delta S = 20$ J/mol K. These theoretical estimates are larger than experimental data: $\Delta S = 10$ J/mol K, $S(T_v+0) = 13$ J/mol K, $S(T_v-0) = 3$ J/mol K. [19] However, the theoretical estimate of the ratio $S(T_v+0)/S(T_v-0) = 5.1$ is in good agreement with the experimental value $S(T_v+0)/S(T_v-0) = 4.3$. Below $T_v$ $f$ holes are strongly hybridized with conduction band holes and form the nonmagnetic heavy fermion Fermi-liquid ground state. That is why the entropy tends to zero in the limit $T \rightarrow 0$.

There are a few reasons of the divergences between our estimates and experimental data.. At first, we neglected a crystal field splitting of the 8-fold degenerate $f$ level. Inelastic neutron measurements [45] revealed that the quartet $\Gamma_8$ is the ground state, but the splitting $\Delta_c$ is quite small, $\Delta_c = 32$ K. The experimental value $S(T_v + 0) = 13$ J/mol K$\approx R \ln 5$ is close to the value $R \ln 4$ expected for four-fold degenerate $\Gamma_8$ state. An account of the crystal-field splitting within our approach will result in decreasing entropy and a more remarkable temperature dependence of the entropy above $T_v$. At second, the mean field approach does not give a correct result of the entropy of the localized $f$ electrons in the high temperature phase. Namely, the approach results in the value $S = R(\ln N - (N - 1)\ln(1 - N^{-1}))$ for the entropy of noninteracting $f$ holes instead of the value $R \ln N$. To obtain a correct result it is necessary to go beyond the mean-field solution and take into account fluctuation corrections in next orders in $1/N$.

In the HF phase at $T << T_v$ the linear coefficient of the specific heat $\gamma$ is given by the relation $\gamma = \frac{1}{3}\pi^2 k_B^2 N \rho_F^*$ where $\rho_F^*$ is determined by Eq.(67). For the parameters

chosen we find $\gamma = 71$ mJ/mol K$^2$. The experiment [19] gives slightly smaller value $\gamma \approx 50$ mJ/mol K$^2$.

### 2. Magnetic susceptibility of YbInCu$_4$

Using Eq.(65) we calculated the temperature dependence of the spin susceptibility $\chi(T)$. Corresponding results are represented in Fig.6. Above $T_v$ localized $f$ electrons give the main contribution into the susceptibility. As a result, the $\chi$ follows the Curie-Weiss law: $\chi = C/T$. Below $T_v$ hybrid quasiparticles are formed, and the electron system under consideration behaves as a Fermi-liquid system with an enhanced Pauli susceptibility. At zero temperature the $\chi(0)$ is given by Eq.(66). At ambient pressure we found $T_L \equiv C/\chi(0) = 384$ K. The experimental value is 470 K. [11] We calculated also the low temperature Kondo scale $T_0$ defined by Eq.(38) and found $T_0 = 315$ K. In the conventional HF systems it is the $T_0$ that plays the role of a universal energy scale for low temperature thermodynamic and transport phenomena in the HF state (see Refs. [30] and [46], for example). According to Eq.(69), in the limit $\mu_0 >> T_0$ there is a simple relation between $T_0$ and $T_L$ : $T_0 = N_f T_L = (1 - \Delta N_f) T_L$. The approximate relation at $\Delta N_f = 0.27$ gives $T_L= 430$ K that is slightly larger than our calculated value ($T_L = 384$ K). The difference is a consequence of the approximate character of the relation, because in our analysis we have $\mu_0/T_0 \sim 2.2$ due to the small hole concentration $N_{0c} = 0.069$ per $f$ ion. Our calculations revealed that both the $T_L = 384$ K and $T_0 = 315$ K are much larger than the Kondo temperature $T_k = 40.4$ K characterizing Kondo effect at $T > T_v$. The result is in agreement to inelastic neutron scattering measurements [45,47,48] that also revealed an enhancement of the energy scale from $T_k = 25$ K to $T_0 = 405$ K. The very large enhancement of $T_0$ in comparison with $T_k$ is brought about by the enhancement of the exchange energy $J$. In papers [11,12] in order to explain the enhancement of $T_L$ it was suggested that the effect is caused by a strong energy dependence of the conduction band DOS $\rho(\varepsilon)$. Namely, $\rho(\varepsilon_F)$ must be sharply increasing function of the Fermi energy $\varepsilon_F$. The results of our calculations show that in terms of the extended lattice Anderson model the enhancement can be explained even in the case of a flat conduction band.

The enhancement of $\gamma$ and $\chi(0)$ with respect to the values typical for normal metals is explained by the increase of the DOS on the Fermi surface. According to Eq.(67), there is also a quasiparticle mass enhancement. Our calculations give $m^*/m_0 = 27$. Therefore, one can classify YbInCu$_4$ as a "light" heavy-fermion compound as it was suggested by Felner et al. [9]

11

### 3. Volume expansion and bulk modulus in YbInCu₄

In Fig.7 we represent results of the numerical calculations of the volume strain $e_B = \Delta v/v$. In good agreement with experimental data [9,11,44] we find a sharp volume expansion about 0.5% when decreasing $T$ below $T_v$. Calculating the volume strain at different pressures, we estimated the isothermal compressibility $k_T = -d\ln v/dP$ and found $k_T(T = 20\text{ K}) = 1.05$ Mbar$^{-1}$. Experimental measurements [44] gave $k_T(T = 20\text{ K}) = 1.2$ Mbar$^{-1}$. Ultrasonic studies [43,49] resulted in $k_T(T = 20\text{ K}) = 0.95$ Mbar$^{-1}$.

Using Eq.(54) we calculated the temperature dependence of the bulk modulus $c_B = 1/k_T$. These results are presented in Fig.8. Such a temperature behavior is in complete agreement with the experimental data. [43,49]

According to Eq.(50), at a sufficiently small electron-lattice coupling the volume strain must be proportional to $\Delta N_f$: $e_B = a\Delta N_f$. Our calculations conform the relation and give $a$=0.019. The experimental estimation of the linear coefficient $a$ is 0.046. [11]

### 4. Pressure effect in YbInCu₄

The effect of pressure on the physical properties of the system under consideration is represented in Fig.6. According to our calculations, applying pressure shifts the critical temperature $T_v$ of the first-order phase transition to lower temperatures at the rate $dT_v/dP = -0.13$ K kbar$^{-1}$. The theoretical estimate is one order of magnitude smaller than the experimental result [10,19,44] , $-2.2$ K kbar$^{-1}$. In order to improve the result, it is necessary probably to go beyond the mean-field theory. Pressure results in decreasing the valence change at the rate $d\Delta N_f(3.5\text{ K})/dP = -6.3$ Mbar$^{-1}$ in a satisfactory agreement with the experimental value $-4.5$ Mbar$^{-1}$ found from volume expansion measurements. [44] In Fig.6 we plot magnetic susceptibility at ambient pressure and $P = 3$ kbar. From the results we find $dT_L/dP = -12.7$ K/kbar in good agreement with the experimental value $-12.4$ K/kbar obtained by Sarrao et al. [19] The theoretical estimate of the Grüneisen parameter $\Gamma = -d\ln T_L/d\ln v = -31$ is in excellent agreement with the experimental value [19] $\Gamma = -30.6$. The physical origin of the pressure effect is related mainly to the influence of pressure on fluctuations of the $f$ shell size. Indeed, an applied pressure decreases volume, $e_B < 0$. In turn, this results in decreasing the exchange interaction $J$ (see Eq.(48)) and, consequently, decreasing the Kondo scales $T_k$ and $T_0$. We believe that the $f$-shell-size-fluctuation mechanism explains also the negative $\Gamma$ observed in other Yb based HF compounds and their pressure dependent properties (see, for example, Ref. [52] and reference therein).

### 5. $H - T$ phase diagram.

Basing on the results of Sec. V we investigated the effect of a magnetic field on the first-order valence phase transition. Only the Zeeman energy was taken into account in the numerical calculations. In our calculations we took the gyromagnetic factor $g = 8/7$ expected for $j = 7/2$. For the sake of simplicity we neglected the electron-lattice interaction, as it gives only about 10% correction in accordance to our estimates. Solving self-consistently Eqs.(59)-(61) we found that magnetic field pushes the first-order valence phase transition to lower temperatures. The obtained $T - H$ phase diagram is represented in Fig.9. It is interesting to note that the elliptic equation

$$\left(\frac{H_v(T)}{H_v(T=0)}\right)^2 + \left(\frac{T_v(H)}{T_v(H=0)}\right)^2 = 1 \qquad (71)$$

is a good fit to the critical line of the first-order phase transition $H_v(T)$ given by our numerical calculations. Recently the relationship Eq.(71) between $H_v(T)$ and $T_v(H)$ was inferred from magnetoresistance measurements. [53] Our estimate of the critical field $H_v(T = 0) = 47$ T is also in a satisfactory agreement with experimental value $H_v(T = 0) = 34$ T. The critical line $H_v(T)$ divides $H - T$ plane into the low temperature-low magnetic field region in which the system is in the mixed-valence heavy fermion ground state, and the high temperature-high magnetic field region in which the system is in a normal state with stable magnetic moments of Yb ions.

### 6. Electrical resistivity and the Hall effect in YbInCu₄

In accordance to the measurements [14,22] the electrical resistivity $R(T)$ in YbInCu₄ demonstrate two peculiarities: (i) a large drop at $T = T_v$ and (ii) a weak temperature dependence at $T < T_v$. Analyzing the data at $T > T_v$, one can distinguish two main contributions into the resistivity: a large residual resistivity $R_0$ and a linear temperature dependent contribution given by electron scattering off phonons. At $T = T_v$ the phonon contribution is much smaller than $R_0$ and as a result $R(T_v + 0) \approx R_0$. In the low temperature phase the residual resistivity $R_0^*$ is approximately 12 times smaller than $R_0$.

Basing on our approach let us analyze the temperature behavior of the resistivity at $T < T_v$. At first, one can note that in the HF state the renormalized electron-phonon interaction is very small and its contribution into resistivity can be neglected (see, for example, Ref. [39]). Only impurity scattering and collisions between heavy fermions determine the resistivity. It leads to $R^*(T) = R_0^* + A^*T^2$, where the coefficient $A^* \sim T_0^{-2}$. [54,55,46]. Since $T_0 >> T_v$, the temperature dependence

of $R^*(T)$ must be weak enough, which is in agreement with the experimental data. [14,22]

Let us estimate and compare the residual resistivity above and below $T_v$. At $T > T_v$ the residual conductivity can be estimated using the well known relation

$$\sigma_0 \sim e^2 \rho_{0F} v_{0F}^2 \tau_0 \sim e^2 N_{0c} \tau_0 \qquad (72)$$

where $v_{0F} = p_{0F}/m_0$ is the Fermi velocity, $p_{0F}$ is the Fermi momentum, $\rho_{0F} \sim p_{0F} m_0$ is the conduction band DOS, $\tau_0^{-1}$ is a rate of a potential scattering of charge carriers off impurities and lattice imperfections. Here we also used that $N_{0c} \sim p_{0F}^3$. In the HF state the residual conductivity is determined by a potential scattering of heavy fermions and is given by a similar equation with the replacement of $\rho_{0F}$, $v_{0F}$, $p_{0F}$ and $\tau_0$ by the renormalized parameters $\rho_F^* \sim p_F m^*$, $v_F = p_F/m^*$ and $\tau^* = \tau_0 m^*/m_0$. [46,56] Moreover, it is necessary to take into account that the renormalized Fermi surface determined by the total number of charge carriers $N_t = N_{0c} + N_{0f}$, that is $((p_F/p_{0F})^3 = N_t/N_{0c})$. Then, we find the residual conductivity at $T < T_v$ :

$$\sigma^* \sim e^2 \rho_F^* (v_F)^2 \tau_0^* \sim e^2 N_t \tau_0. \qquad (73)$$

Therefore, we have $R_0/R_0^* \simeq N_t/N_{0c}$. Above we have found $N_t = 1.07$ while $N_{0c} = 0.07$. It gives the crude theoretical estimation $R_0/R_0^* \simeq 15$ in agreement with the experimental value [22], $R_0/R_0^* \simeq 12$. Thus, we can conclude that the drop of the resistivity and change of its temperature behavior when transiting into the low temperature mixed-valent state in YbInCu$_4$ are mainly related to (i) the decrease of the residual resistivity due to increase of the charge carrier concentration and (ii) the suppression of the electron-phonon scattering.

Basing on our approach one can explain also the jump of the charge carrier concentration at $T = T_v$ observed in the Hall measurements. [11,12] Indeed, at $T > T_v$ $f$ electrons are localized and only conduction band holes with the concentration $N_{0c}$ participate in transport phenomena and the Hall effect. At $T < T_v$ the $f$ electron states are hybridized with conduction band states, which results in the formation of hybrid quasiparticles (heavy fermions). The total number of the quasiparticles under the renormalized Fermi surface is equal to $N_t > N_{0c}$. All these quasiparticles give a contribution into the Hall constant.

### B. Physical properties of YbAgCu$_4$

As we have discussed above, with decreasing the interaction $U_{cf}$ the system under consideration reveals a crossover from the first-order valence phase transition to a continuous formation of the HF state. We use such a scenario for describing thermodynamic properties of YbAgCu$_4$. In many respects YbAgCu$_4$ is close to YbInCu$_4$, but YbAgCu$_4$ has a normal metallic charge carrier concentration. For our calculations we take $N_{0c}=0.21$ per Yb, which corresponds to 0.84 charge carrier per unit cell. The best fitting to the experimental data is found at the following parameters: $V = 0.24$ eV, $1/N\rho_0 = 0.9$ eV, $\mu_0 - E_f = 0.25$ eV which are close to ones for YbInCu$_4$. Only the interaction $U_{cf} = 0.276$ eV is taken almost twice smaller than $U_{cf}$ in YbInCu$_4$. The small value of $U_{cf}$ can be explained by a stronger charge screening due to a larger charge carrier concentration in comparison to YbInCu$_4$. For these parameters we have $N\rho_0 V^2 = 0.064$ eV, $\mu_0 = 0.19$ eV. The value of $4f$ level energy is consistent with the result of PES [50,51], 0.3 eV.

For describing the electron-lattice interactions in YbAgCu$_4$ we use the same $r$ and $d$ as for YbInCu$_4$, i.e. $r = -2$, $d = 2$ eV, and $C_B = 1,03 \times 10^{-10}$ erg. For the parameters chosen the equations (32)-(34) and (55) have only one nontrivial (conventional-like) solution below $T_k = 86$ K. Results of numerical calculations based on the solution are represented in Figs.3-8.

Let us compare temperature behavior of YbAgCu$_4$ and YbInCu$_4$. In accordance to our numerical calculations the HF state in YbAgCu$_4$ is continuously formed below $T_k = 86$ K. This temperature correlates with the temperature of the resistance maximum, $T_{max} \approx 75 - 90$ K. [22] According to our calculations represented in Fig.4, at $T \to 0$ the valence change $\Delta N_f$ tends to 0.13 in very good agreement with the $L_3$ data [11].

Temperature behavior of the entropy is represented in Fig.5. Unfortunately, entropy measurements in YbAgCu$_4$ are unknown for us to be compared with our calculations. The calculated value of the linear coefficient of the specific heat $\gamma = 230$ mJ/mol K$^2$ is between the data [11] $\gamma = 220$ mJ/mol K$^2$, and $\gamma = 250$ mJ/mol K$^2$ found from other measurements. [22]

The calculated magnetic susceptibility $\chi(T)$ represented in Fig.6 has a broad maximum at $T \approx 40$ K and its maximum value is approximately twice smaller than $\chi(T = T_v)$ in YbInCu$_4$, which is in good agreement with the magnetic measurements. [22] The calculated value $T_L = 120$ K is slightly smaller than the experimental data [11,22] $T_L = 150$ K.

The calculated mass enhancement in YbAgCu$_4$ is equal to $m^*/m_0 = 87$ . This value is in three times larger then the mass enhancement in YbInCu$_4$. Therefore, one can classify YbAgCu$_4$ as a "moderate" heavy-fermion compound.

The temperature dependence of the volume strain $e_B$ is shown in Fig.7. In YbAgCu$_4$ the zero temperature value $e_B(T = 0) = 0.24$ % is approximately twice smaller than the $e_B(0)$ in YbInCu$_4$. We find that the relation $e_B = a\Delta N_f$ holds also in YbAgCu$_4$ with $a = 0.018$.

Using the parameters given above we calculated the temperature behavior of the bulk modulus for two concentrations of charge carriers, $N_{0c}=0.21$ and $N_{0c}=0.07$. In the both cases the calculations revealed a minimum of the bulk modulus. These results are represented in Fig.8. One can see that with increasing the charge car-

rier concentration the minimum becomes smaller and less expressive. The results of our calculation for $N_{0c}$=0.07 can be related to the behavior of the bulk modulus of $YbIn_{1-x}Ag_xCu_4$ at $x \approx 0.3$, [49] because in the case the charge carrier concentration is still small but the system already shows a continuous transition into the HF state. [22] The calculated behavior of the bulk modulus represented in Fig.8 is in good agreement, both qualitative and quantitative, with the acoustic measurements. [49]

## VII. DISCUSSION AND CONCLUSIONS

In the present section we shall discuss the mean-field approximation used in our paper and other problems related to physical phenomena in $YbIn_{1-x}Ag_xCu_4$, and summarize results of our numerical calculations performed in the framework of the extended lattice Anderson model proposed in the present paper.

Our consideration of the model was based on the mean-field approximation that corresponds to taking into account the leading order of the $1/N$ expansion. The mean-field solution is the exact solution of the extended lattice Anderson model in the limit $N \rightarrow \infty$. In the case under consideration the degeneracy $N$ of the electron state $4f^{13}$ is finite and equal to 8. Therefore, we face the problem of fluctuations around the mean-field solution. The fluctuations give $1/N$ corrections to the solution. Unfortunately, so far there is no a detail analysis of the corrections into thermodynamic properties of the lattice Anderson model. There is only an exact solution of the single-impurity Anderson model with Hamiltonian Eq.(1) for arbitrary degeneracy $N$. [37] In the paper [37] it has been shown that in the Fermi-liquid regime at $T << T_0$ the magnetic susceptibility and heat capacity given by the mean-field solution are in a remarkably good quantitative agreement with the exact solution even for $N = 2$. For $N = 8$ the region of a quantitative agreement becomes broader. A noticeable error occurs only around the crossover from weak to strong coupling ($T \sim T_k$) where the critical fluctuations of the slave-boson field about the mean-field solution are greatest. However, a qualitative agreement takes place even in the region. With increasing temperature above $T_k$ the mean-field solution converges quickly to the exact solution, as both solutions describe a paramagnetic state with localized $4f$ electrons that weakly interact with conduction band electrons. As shown in [57] at high temperatures, the impurity susceptibility approaches Curie behavior with logarithmic corrections of order $O(1/N)$ that are produced by slave-boson fluctuations around the normal state.

There is the only significant defect of the mean-field solution related to the fact that in the limit $N \rightarrow \infty$ the crossover from weak to strong coupling sharpens into a second order phase transition at $T_k$. Besides, at $T = T_k$ the susceptibility has a break in the temperature dependence.

Basing on the results let us consider the extended lattice Anderson model. In the framework of the mean-field approach both the single-impurity and lattice Anderson models are described by the same order parameter (see Eq.(19)). However, unlike the single impurity model, the lattice model contains spatial correlations of the order parameter. It is well known from the theory of critical phenomena that with increasing the dimensionality, order parameter fluctuations become weaker. Therefore, one can expect that critical fluctuations in the 3D lattice model around the mean-field solution are not stronger than the fluctuations in the single-impurity model studied in the paper [37].

From this point of view let us discuss our mean-field solutions for compounds $YbInCu_4$ and $YbAgCu_4$. According to the experimental data [11,45,47,48] and our calculations, the low temperature Kondo scale $T_0$ is about 400K in the low temperature phase of $YbInCu_4$, that is below $T_v = 42$ K. As $T_v << T_0$, one can expect that at $T < T_v << T_0$ fluctuations around the mean-field solution are weak and give small corrections with respect to small parameters $1/N$ and $T/T_0$. We think that it explains a good agreement between experimental data and our numerical calculations of susceptibility, entropy, valence change of Yb ions, volume change, bulk modulus and other physical parameters presented in Sec. VIA. At temperatures $T > T_v$ we are in the regime $T > T_v > T_k = 25$ K, therefore, we again expect that corrections of order $O(1/N)$ due to slave-boson fluctuations around the normal state are small and become noticeable only at $T$ close to $T_v$. As at these temperatures there are no correlations between Kondo scattering of electrons off different localized $f$ electrons, $1/N$ corrections to thermodynamic properties are the same as in the single-impurity Anderson model.

In $YbAgCu_4$ we have a similar situation. We expect that at low temperatures $T << T_0 = 150$ K the mean-field solution gives a good description of thermodynamic properties. The maximum error occurs in the crossover region with $T_k = 86$ K. It is interesting to note that according to our numerical calculations, in the lattice case the break of temperature behavior of $\chi(T)$ at $T_k$, which is an artifact of the mean-field approximation, is very small in comparison to the mean-field solution of the single-impurity Anderson model [37].

In order to check the mean-field solution of the lattice Anderson model Eq.(1) one could use the dynamical mean-field theory that at the present time attracts much attention. [58] For the purpose in terms of the theory it is necessary to solve the model Eq.(1) at different degeneracy $N = 2, 4, 6, 8...$, and then to compare the solutions with the mean-field solution based on the $1/N$ expansion as it has been done for the single-impurity Anderson model [37]. Unfortunately this problem is still open and is out of the scope of the present paper.

Above we have mentioned that in accordance to the Hall measurements [11,12] in compounds $YbIn_{1-x}Ag_xCu_4$ at $x < 0.2$ the charge carrier concen-

tration is low, 0.07 per formula unit. However, neutron scattering [47] and susceptibility measurements [22] can be well interpreted in terms of the single-impurity Anderson model with a metallic electron concentration. It enables us to conclude that in the compounds the charge carrier concentration is larger than that concentration at which it would be necessary to take into account Nozières exhaustion principle. In the case $x > 0.3$ the charge carrier concentration quickly achieves a normal metallic concentration, and the problem of a low charge carrier concentration already does not confront before us.

The $L_3$ measurements [11] in YbInCu$_4$ give a clear evidence for a non-integral valence of Yb ions in the normal state. However there is a profound difference between the origin of the non-integral valence of Yb ions above and below $T_v$. In the high temperature region ($T > T_k$) the non-integral valence of Yb ions is produced by uncorrelated electron transitions between the $f$ shell of a Yb ion and conduction band. The transitions do not breakdown the localized character of $f$ electron states. Certain correlations due to the Kondo effect arise only when the temperature lowers to temperatures about $T_k$. As we have shown above within our approach, at $T < T_v$ the mixed valence state of Yb ions is caused by the effective hybridization between $4f$ and conduction band states, which results in a renormalization of the conduction band and the formation of hybrid quasiparticle states due to the coherent Kondo effect. In other words, one can say that at $T < T_v$ the electron transitions become strongly correlated. From this point of view the change of the Yb ion valence is related to the change of the spatial electron distribution over electron states of all ions, including Cu and In ions, participating in the formation of the renormalized conduction band, which is consistent with the NQR and Knight shift measurements [15–18]. This physical picture is also consistent with the theory of the mixed-valent state formation for a single Kondo impurity in terms of the single impurity Anderson model (see, for example, [30,31]).

There is another interesting problem related to the crystal field splitting of the degenerate $4f$ level in YbInCu$_4$. The inelastic neutron scattering measurements [45] have revealed a crystal-field (CF) splitting of order 32 K in high temperature phase. Below $T_v$ the CF excitations disappear. Recently the effect of the hybridization on the CF splitting was also observed in certain Ce based compounds of type ReNi by use of neutron spectroscopy [59] at temperatures below $T_k$ in the Fermi-liquid regime. Therefore, one can suppose that the hybridization and formation of the heavy fermion ground state at $T < T_v$ also influence the temperature behavior of the CF excitations in YbInCu$_4$.

The theory of the first order valence phase transition developed in the present paper can be applied also for studying valence transitions in Ce based and other rare earth compounds. Specifically, recent measurements [60] on Ce alloyed with 7 at.% Sc to stabilize the $\gamma-$Ce phase against $\beta-$Ce formation demonstrated a similar physi-

cal behavior at the $\gamma - \alpha$ isostructural first-order phase transition as the behavior observed in YbInCu$_4$, namely, localized $f$ electrons in $\gamma-$Ce and delocalized ones in $\alpha-$Ce, a valence change $\Delta N_f \approx 0.2$, a large enhancement of the Kondo scale from $T_k \sim 60$ K in $\gamma-$Ce to $T_0 \sim 1800$ K in $\alpha-$Ce and so on. However, according to experimental data, the electron-lattice coupling in Ce based compounds is stronger than this coupling in Yb compounds and can be a driving force of the transition. [26,27]

In summary, we have used the extended lattice Anderson model for investigating the first-order valence phase transition in YbInCu$_4$. The model takes into account Coulomb repulsion $U_{cf}$ between $f$ and conduction band holes, and two mechanisms of the electron-lattice interaction. For the model we have developed a mean-field approach based on the $1/N$ expansion method. Within the mean-field approach we have found that the system under consideration undergoes a first-order phase transition from the normal state into the heavy-fermion state with mixed valent $f$ ions. We have found that the Coulomb interaction $U_{cf}$ strongly influences on the exchange interaction $J$ between spins of $f$ and conduction band electrons. The $U_{cf}$ enhances $J$ and, as a result, the coherent Kondo effect is also enhanced. It is the driving force of the first-order valence phase transition. Basing on the model, we have carried out numerical calculations of temperature and pressure dependences of thermal, magnetic and elastic properties of YbInCu$_4$ and obtained a good agreement with experimental results. We have studied the role of the electron-lattice coupling in the compound and found that the $f$ shell-size-fluctuation mechanism of the electron-lattice interaction gives the main contribution into the volume change of the lattice and determines the negative sign of the Grüneisen parameter. Our analysis have shown that the evolution of the first-order phase transition into a continuous transition in the series of compounds YbIn$_{1-x}$Ag$_x$Cu$_4$ can be explained by decreasing the interaction $U_{cf}$ with increasing Ag concentration $x$ due to increase of the charge carrier concentration and an enhancement of charge screening. In the framework of the extended Anderson model we have found that a magnetic field pushes the valence transition to lower energies, and in the $H - T$ plane the critical line of the first-order valence phase transition is described by an elliptic equation in complete agreement with experimental data

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FIG. 1. Order parameter (the effective hybridization) $B$ versus $T$. The conventional solution of the mean-field equations Eqs.(32)-(34) for the interaction $U_{cf} = 0$ is given by the dotted curve. Curves $s$ and $h$ represent "soft"and "hard" solutions of the equations, respectively, at a moderately large $U_{cf}$ ($U_{cf} = 0.451$ eV, $N = 8$, $V = 0.267$ eV, $N\rho_0$=1.125 eV$^{-1}$, $N_{0c}$=0.069 per formula unit, $\mu_0 - E_f = 0.272$ eV) when $T_k/\mu_0 = 0.057$ and $T_v/\mu_0 = 0.055$. Here the electron-lattice interaction is neglected.

FIG. 2. Free energy $F$ of the extended lattice Anderson model as a function of the order parameter (the effective hybridization) $B$ at different temperatures $T/\mu_0$ =0.04, 0.05, 0.06, 0.07 for the same parameters $V, N, N\rho_0$ and $N_{0c}$ as those in Fig.1 ($T_k/\mu_0 = 0.057$, $T_v/\mu_0 = 0.055$). A deep minimum arising at temperature $T/\mu_0 \lesssim 0.06$ and $B$ near 2 corresponds to the "hard" solution. The arrow shows the position of a minimum of the $F$ corresponding to the "soft" solution.

FIG. 3. Temperature dependence of the free energy $F$ in the normal state (curve 1) and the heavy-fermion (HF) state (curve 2) in YbInCu$_4$ and YbAgCu$_4$. In YbInCu$_4$ the HF state is described by the hard solution of the mean-field equations while in YbAgCu$_4$ it is described by the covential solution. The free energies are given with the accuracy up to a certain energy shift.

FIG. 4. Valence change ($\Delta N_f$) versus temperature $T$ in YbInCu$_4$ (curve 1). Curve 2 shows the $\Delta N_f$ in the case when the electron lattice interaction is neglected. Curve 3 is the $\Delta N_f$ in YbAgCu$_4$. Curve 4 is the $\Delta N_f$ in the case when both the electron-lattice coupling and the on-site Coulomb repulsion $U_{cf}$ are neglected.

FIG. 5. Temperature dependence of the entropy $S(T)$ in YbInCu$_4$ (solid curve) and in YbAgCu$_4$ (dotted curve).

FIG. 6. Magnetic susceptibility $\chi$ versus temperature $T$ in YbInCu$_4$ at pressure $P = 0$ (curve 1) and $P = 3$ kbar (curve 2). Curve 3 is the $\chi$ in YbAgCu$_4$ at $P = 0$ and $T_k = 86$K. Curve 4 is the $\chi$ for the same parameters as for YbInCu$_4$ but when both the electron-lattice coupling and the Coulomb interactions $U_{cf}$ are neglected.

FIG. 7. Volume strain $e_B$ against $T$ in YbInCu$_4$ (solid curve) and in YbAgCu$_4$ (dotted curve).

FIG. 8. Bulk modulus $c_B$ versus $T$ in YbInCu$_4$ (solid curve), YbAgCu$_4$ (dotted curve) and YbIn$_{0.7}$Ag$_{0.3}$Cu$_4$ (dash-dotted curve).

FIG. 9. Normalized critical magnetic field $H_v(T)/H_v(T = 0)$ versus the normalized temperature $T/T_v(H = 0)$ in YbInCu$_4$. Results of the numerical calculations are presented by solid squares. The critical line of the first-order valence phase transitions divides the $H - T$ phase diagram of into two regions corresponding to the mixed-valence heavy fermion (HF) state and a normal paramagnetic (P) state with stable magnetic moments. The elliptic equation (71) (dotted curve) is a good fit to the critical line.